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Abstract

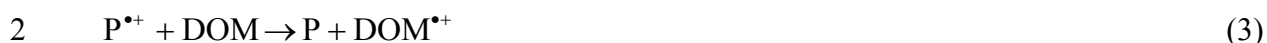
Dissolved organic matter (DOM) has recently been shown to reduce the transformation rate of various aqueous organic contaminants submitted to oxidation by excited triplet states, apparently by inhibiting the transformation of oxidation intermediates. The main goals of the present study were to evaluate in more detail the effect of concentration and type of DOM on the triplet-induced transformation rate of four selected organic compounds and to check for an analogous inhibition effect in the case of oxidation induced by hydroxyl radical. A marked inhibition by DOM of triplet-induced oxidation was observed for *N,N*-dimethylaniline (DMA) and the two antibiotics sulfamethoxazole (SMX) and trimethoprim (TRI), DOM of terrestrial origin being a more effective inhibitor than DOM of aquatic origin. The results are important to understand the role of DOM both as a photosensitizer and as an inhibitor for the triplet-induced transformation of aquatic contaminants. In contrast, no DOM-induced reduction in second-order rate constant could be observed in competition kinetics experiments for the reaction of hydroxyl radical with a series of 15 organic compounds, covering several classes of aromatic contaminants, indicating that Suwannee River fulvic acid (SRFA) used as reference DOM does not affect this reaction mechanism.

1 **Introduction**

2 The presence of dissolved organic matter (DOM) in natural waters has an important influence
3 on light-induced transformation pathways of organic contaminants. An increased photochemical
4 transformation rate of pesticides in natural waters with respect to pure aqueous solutions was
5 already reported more than three decades ago {Zepp, 1976 #1}. This acceleration of
6 transformation is mainly initiated by the absorption of light by water components such as DOM,
7 nitrate and nitrite ion, and various Fe(III) species, leading to the formation of several primary and
8 secondary reactive species that are able to react with organic compounds {Zafiriou, 1984
9 #81} {Richard, 2005 #5}. Among these species excited triplet states of DOM ($^3\text{DOM}^*$) and
10 hydroxyl radical ($\cdot\text{OH}$) play an important role because they have oxidative reactivity towards a
11 wide range of environmentally relevant compounds ($^3\text{DOM}^*$: {Canonica, 1995 #22; Gerecke,
12 2001 #90; Chin, 2004 #4; Werner, 2005 #3; Boreen, 2005 #13}; $\cdot\text{OH}$: {Haag, 1992 #6; Huber,
13 2003 #8; Esplugas, 2007 #7}). However, DOM can also contribute to decrease the
14 phototransformation rate of contaminants by three distinct effects: Scavenging/quenching of
15 reactive species, filtering/screening (attenuation) of the photochemically active light, and limiting
16 of the net oxidation due to reduction of intermediates.

17 While scavenging of hydroxyl radical {Brezonik, 1998 #87} {Goldstone, 2002
18 #88} {Westerhoff, 2007 #26} and light screening by DOM {Leifer, 1988 #16} have been studied,
19 little is known about the reduction of oxidation intermediates by DOM {Canonica, 2008 #10}.
20 This reduction may be considered as an alternative case of scavenging/quenching, where not the
21 oxidative reactive species itself but a transformation intermediate of the contaminant P reacts
22 with DOM, as exemplified in the following scheme:





3 According to eq 1, an oxidative reactive species RS (e.g., $^3\text{DOM}^*$, $^{\bullet}\text{OH}$) reacts with the
 4 contaminant leading to a reduction product of RS, RS_{red} , and an intermediate radical cation $\text{P}^{\bullet+}$.
 5 Subsequently $\text{P}^{\bullet+}$ undergoes parallel reactions, where it is either irreversibly oxidized to P_{ox} (eq 2)
 6 or reduced back to its parent compound by easily oxidizable moieties of DOM generating an
 7 oxidized $\text{DOM}^{\bullet+}$ species (eq 3). The more the second pathway is favored the smaller the yield of
 8 P_{ox} and consequently the rate of contaminant transformation should be. Reduction of oxidation
 9 intermediates by DOM is plausible {Aeschbacher, 2010 #89} because DOM contains a variety of
 10 organic moieties, in particular phenolic functional groups, which may act as antioxidants. It
 11 should be noted that in the above reaction scheme $\text{P}^{\bullet+}$ stands as a representative for a suite of
 12 possible oxidation intermediates that may be reduced back to the parent compound. A direct
 13 observation of the species involved in eq 3 is still outstanding.

14 An initial study of the possible inhibition of oxidation reactions by DOM {Canonica, 2008 #10}
 15 was carried out using the excited triplet state of benzophenone-4-carboxylate (CBBP) as the
 16 oxidant. The oxidation rate of around half of twenty-two environmentally relevant aquatic
 17 contaminants was found to decline in the presence of Suwannee River fulvic acid (SRFA), used
 18 as a reference DOM. Especially compounds having an aniline functionality, including antibiotics
 19 such as sulfonamides and trimethoprim (TRI), but also some phenols were hindered by DOM in
 20 their transformation. Triplet quenching by DOM was excluded as a possible underlying
 21 mechanism since a significant number of the studied contaminants was not affected by any
 22 reduction in oxidation rate in the presence of DOM. Triplet state quenching would result in a

uniform decrease in oxidation rate for any target contaminant. A simple reaction model was introduced to explain DOM-induced inhibition of oxidation.

The objective of the present study was to further characterize the observed inhibition, to generalize and refine the reaction model and to screen for the occurrence of the effect in an alternative oxidation system. For triplet induced oxidation we selected four target compounds to be oxidized: (i) 4-methylphenol (4MP) as a representative for the compounds for which no inhibition of triplet induced oxidation by DOM was found, (ii) *N,N*-dimethylaniline (DMA), and the two antibiotics (iii) sulfamethoxazole (SMX) and (iv) trimethoprim (TRI) as compounds showing inhibition by DOM. Investigations were extended to consider the influence on oxidation for several types of DOM and a lake water and the use of 2-acetonaphthone (2AN) as a photosensitizer (and excited triplet state precursor) in addition to CBBP. The second photosensitizer was included to have an improved model system for mimicking the oxidative properties of $^3\text{DOM}^*$ {Canonica, 2007 #11}. In additional experiments using competition kinetics, the influence of SRFA on the oxidation of several organic contaminants by $\cdot\text{OH}$ was investigated. Hydroxyl radical was chosen, because of its importance in the aquatic environment, where it is produced photochemically by various pathways {Larson, 1994 #23}, and in water treatment processes such as ozonation and advanced oxidation (AOPs) {Hoigné, 1998 #24}.

Experimental Section

Materials and chemicals. All chemicals were from commercial sources and used without further purification. For a complete list of chemicals used see the Supporting Information (SI), Text S1. Standard DOMs: Nordic Aquatic Fulvic Acid (NAFA), Pony Lake Fulvic Acid (PLFA),

and Suwannee River Fulvic Acid (SRFA) were obtained from the International Humic Substances Society. Lake water (GSW) was collected at lake Greifensee, Switzerland ([DOM] = 3.9 mgC L⁻¹; pH 8.0), immediately filtered (0.45 µm, cellulose nitrate, Sartorius AG, Goettingen, Germany) and stored in glass bottles in the dark at 4°C.

Irradiation experiments. Steady state irradiations were performed in glass-stoppered quartz glass tubes using a merry-go-round photoreactor equipped with a medium-pressure mercury lamp operated at 500 W and appropriate filters. Details about the irradiation procedures are given in SI, Text S2. Prior to irradiation, solutions were aerated and equilibrated for 15 min in a water bath at a temperature of 25.0 °C, which was kept constant (± 0.2 °C) during irradiation.

The oxidation of contaminants and model compounds (in the following both referred to as target compounds) by ³Sens* in the presence of standard DOM and GSW was investigated by irradiating up to six tubes simultaneously. Solutions containing standard DOM were buffered at pH 8 with 5 mM phosphate (Na₂HPO₄/NaH₂PO₄) and adjusted with H₂SO₄. GSW was not further treated, prior to irradiations. Each tube was filled with 20 mL GSW or standard DOM solution at 0 – 5 mgC L⁻¹ (except the combination CBBF-TRI-PLFA: 0 – 8 mgC L⁻¹) and supplemented with a target compound at a concentration of 5 µM and an aromatic photosensitizer at a concentration to obtain 5% – 80% depletion during irradiation time. (Target compound/[CBBP]/[2AN]: 4MP/40 µM/150 µM; DMA/40 µM/20 µM; SMX/40 µM/ 70 µM; TRI/40 µM/200 µM). Solutions were irradiated for 5 min. To determine phototransformation rates in “blank” samples, i.e. samples without a model photosensitizer, a set of tubes containing 5 µM of target compound in buffered water, GSW or buffered standard DOM solutions was irradiated for 20 – 120 min, based on the depletion rate of the target compound (4MP: 20 min; DMA 60 min; TRI: 120 min; SMX:

120 min). Samples of 400 μL were withdrawn at six equidistant time intervals and analyzed immediately or stored at 4°C.

For $\cdot\text{OH}$ competition kinetics experiments, performed based on hydrogen peroxide photolysis and using a procedure described elsewhere {Huber, 2003 #8}, a set of four tubes was irradiated for each target compound. Besides borate buffered solution (5 mM, pH 8) with 0.5 μM of target compound and 0.5 μM *p*-chlorobenzoic acid (*p*CBA), these tubes contained (i): no additions; (ii): 2.5 mgC L^{-1} SRFA; (iii): 5 mM H_2O_2 ; (iv): 2.5 mgC L^{-1} SRFA and 5 mM H_2O_2 . Six samples were taken during 20 min of irradiation.

Analytical methods. A description of the HPLC systems used to examine depletion of target compounds including a complete list of HPLC conditions, detection wavelengths and separation columns is given together with details of spectrophotometric and pH-measurements in SI, Table S1 & Text S3.

Results and Discussion

A. Triplet-induced oxidation

Kinetics analyses and corrections. The inhibition of oxidation of target compounds was quantified by means of kinetics experiments, where the initial concentrations of the selected target compound and photosensitizer were kept constant, while the DOM concentration was varied. For each concentration of selected DOM two kinetics runs were carried out with and without the selected photosensitizer, respectively. As already pointed out previously {Canonica, 2008 #10}, the blank experiments, i.e. those conducted in the absence of a photosensitizer, serve to introduce some inevitable correction to compensate for direct and indirect phototransformations of the target compound which do not depend on the photosensitizer. Data

were analyzed by linear regression using the logarithmic form of the pseudo-first-order kinetic equation: $\ln(\frac{C}{C_0}) = -k \cdot t$, where C and C_0 are the concentrations of target compound at irradiation time t and zero (before irradiation), respectively, and k (s^{-1}) is the pseudo-first-order rate constant. A set of such regression lines is shown in SI (Figure S1).

In general, photoinduced transformation in the absence of both photosensitizer and DOM, possibly arising from direct phototransformation and indirect phototransformation induced by impurities, k_{blank} , were found to be negligible. DOM alone, which is well known to possess photosensitizing activity {Richard, 2005 #5; Canonica, 2008 #10}, induced significant depletion of the target compound in some cases. Thus, rate constants for the transformation of target compound in the presence of a photosensitizer and DOM, $k_{Sens,DOM}([DOM])$, were corrected by applying eq 4.

$$k_{Sens,DOM}^{(1)}([DOM]) = k_{Sens,DOM}([DOM]) - k_{DOM}([DOM]) \quad (4)$$

where $k_{DOM}([DOM])$ is the target compound transformation rate constant obtained in the absence of photosensitizer and $k_{Sens,DOM}^{(1)}([DOM])$ is the corrected rate constant (note that for the case of absence of DOM, $k_{Sens,DOM}([DOM] = 0) = k_{Sens}$ and $k_{DOM}([DOM] = 0) = k_{blank}$, leading to $k_{Sens}^{(1)} = k_{Sens} - k_{blank}$). The superscript ⁽¹⁾ indicates the first of two subsequent correction steps. Experimental conditions were chosen in order to minimize the DOM-photosensitized transformation of target compounds making only a small correction necessary. Data for k_{Sens} , $k_{DOM}([DOM] = 5 \text{ mgC L}^{-1})$ and k_{blank} are given in SI, Table S3. Generally, using CBBP at a concentration of 40 μM the maximum correction introduced by eq 4 amounted to 10%. Corrections when using 2AN were in some cases higher, due to the slower transformation obtained with some target compounds (especially with TRI).

The second correction step introduced in the analysis of the present data concerns the compensation for the absorption of light by DOM, causing a screening effect or, in other words, a decrease in fluence rate and therefore in light available for the triplet-induced process. The procedure for calculating an approximate light screening factor, $\overline{S}_{\lambda, DOM, Sens}^{rel}([DOM])$, is described in detail in SI (Text S4, Figure S2 and Table S2). This further correction is expressed by eq 5.

$$k_{Sens, DOM}^{(2)}([DOM]) = k_{Sens, DOM}^{(1)}([DOM]) \times \overline{S}_{\lambda, DOM, Sens}^{rel}([DOM]) \quad (5)$$

Although the two corrections according to eqs 4 and 5 are needed for an accurate quantitative data analysis, they do not drastically change the rate constants, and qualitative trends are generally the same for both corrected and uncorrected data. In the following, the superscript ⁽²⁾ indicates that the data shown underwent both correction steps.

Corrected oxidation rate constants: Dependence on DOM concentration. The effect of the presence of DOM on the photosensitized oxidation rate constants of the selected target compounds is shown in Figure 1 for the case of SRFA as a model DOM. For an optimal data representation the corrected rate constants (eq 5) were normalized to the zero-DOM value, i.e. to $k_{Sens}^{(2)} = k_{Sens, DOM}^{(2)}([DOM]=0)$, and plotted as $k_{Sens, SRFA}^{(2)}([SRFA])/k_{Sens}^{(2)}$. For CBBP as the photosensitizer (Figure 1a), the strongest decrease of the oxidation rate could be observed for the pyrimidine derivative TRI. Already an addition of 0.5 mgC L⁻¹ of SRFA led to a decline of 80% in oxidation rate constant. Addition of more than 1 mgC L⁻¹ gave no significant further decrease. A steady decrease in oxidation rate with increasing [SRFA] was found for SMX, with a reaction rate decrease of 70% at 5 mgC L⁻¹ of SRFA. For DMA the decrease in relative rate constant at low [SRFA] was slightly more pronounced than for SMX, but at higher [SRFA] the relative rate constant appeared to level off to reach a limiting value of ≈ 0.5 . In contrast to these three

compounds, the phenolic compound 4MP showed no decreased oxidation rate in the presence of SRFA, as expected from previous results {Canonica, 2008 #10}.

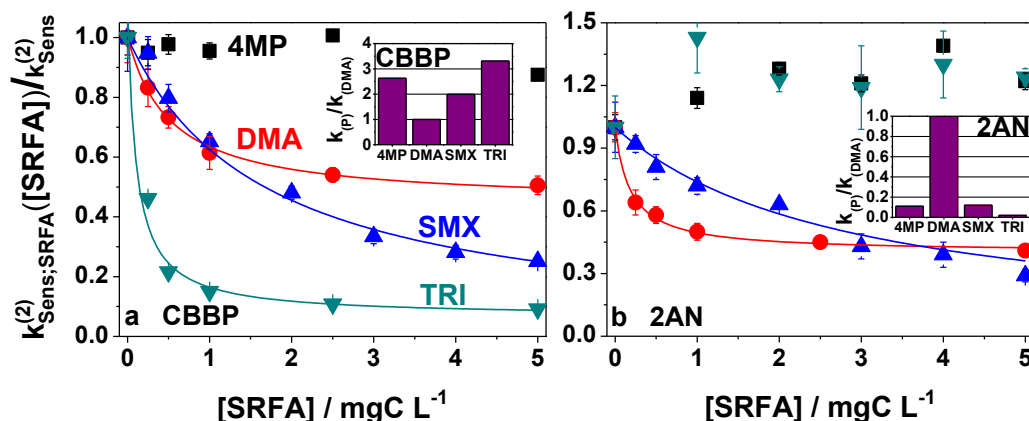


Figure 1. The influence of Suwannee River fulvic acid (SRFA) on the rate constants for oxidation photosensitized by a) CBBP and b) 2AN, for the four target compounds 4MP (■), DMA (●), SMX (▲), and TRI (▼). Error bars indicate 95% confidence intervals. Curves represent non-linear fits to eq 7. Insets: Relative oxidation rate constants of target compounds normalized to DMA in the absence of DOM.

The results obtained using 2AN as the photosensitizer (Figure 1b) are somewhat different from those observed with CBBP. Whereas the trends for DMA and SMX are similar to those shown in Figure 1a, TRI exhibits a completely different behavior, with strong data scattering and even a slight increase in oxidation rate with increasing [SFRA]. The data scattering is due to the very low reactivity of $^3\text{2AN}^*$ towards TRI (Figure 1b, inset), which makes the determination of rate constants inaccurate. The assignment of such a residual TRI reactivity to direct oxidation by $^3\text{2AN}^*$ is uncertain, and a comparison with results obtained using CBBP is not useful. The 4MP-

1 $^3\text{2AN}^*$ data show a moderate increase in oxidation rate with increasing [SRFA], and this
2 contradicts the expectation that the oxidation rate of 4MP should not be affected by DOM. We
3 interpret this enhancement in oxidation rate as being due to the formation of additional oxidative
4 species by interaction of $^3\text{2AN}^*$ with DOM, which would add a further reaction channel for 4MP
5 oxidation.

6 Analogous rate constant diagrams, as shown in Figure 1, are given in SI (Figure S3) for the
7 other two standard DOMs used here, namely NAFA and PLFA. For NAFA patterns are very
8 similar as for SRFA. This common feature is not surprising since both NAFA and SRFA have a
9 strong allochthonous (soil-derived) component. In contrast, PLFA showed a more complex
10 behavior. Trends observed in the system with CBBP and PLFA are almost the same as for the
11 two previous DOMs (the only deviation consists in slightly higher values for the SMX oxidation
12 rate constant at low [PLFA]). In the system with 2AN and PLFA it is hard to recognize a
13 decrease in oxidation rate constant with increasing [PLFA]. On the contrary, the rate constants
14 for 4MP and SMX oxidation are even increased by up to about 50% in the presence of PLFA. As
15 suggested above when discussing the behavior of 4MP in the 2AN-SRFA system, the formation
16 of additional photooxidants by interaction of the excited triplet ketones with DOM appears to be
17 a plausible explanation for the increased depletion rate of the target compounds, and such an
18 effect seems to be stronger for PLFA than for the other two fulvic acids. Such a difference in the
19 behavior of PLFA and the mostly allochthonous fulvic acids is probably connected to their
20 markedly different chemical composition, with lower aromaticity and much higher nitrogen
21 content for PLFA {Guerard, 2009 #80}.

22 To check the transferability of results obtained using standard DOMs to real surface waters,
23 additional experiments were performed using almost undiluted GSW (CBBP systems: 94.5%,
24 2AN systems: >96.8%). Samples of this water were taken from Lake Greifensee, a small

eutrophic lake whose DOM contains predominantly autochthonous but also allochthonous components, and should therefore have intermediate chemical characteristics with respect to NAFA and SRFA on the one hand and PLFA on the other. Figure 2 shows normalized oxidation rates ($k_{Sens,DOM}^{(2)}([DOM])/k_{Sens}^{(2)}$) for GSW and solutions of standard DOM, all containing the same amount of DOM (3.9 mgC L^{-1}). In the case of 4MP the increase of the rate in GSW was found to be higher than for the corresponding amounts of standard fulvic acids (in terms of carbon). This indicates that the already proposed formation of additional photooxidants is more efficient in the lake water than in DOM solutions (possibly due to the presence of anions such as carbonate/bicarbonate and nitrite). For the other three target compounds, the extent of inhibition of oxidation for GSW was similar to the studied DOM solutions, but was not always intermediate with respect to the studied autochthonous and allochthonous DOM. The only deviation from this general behavior was found for the system SMX/CBBP, where inhibition in GSW was almost negligible.

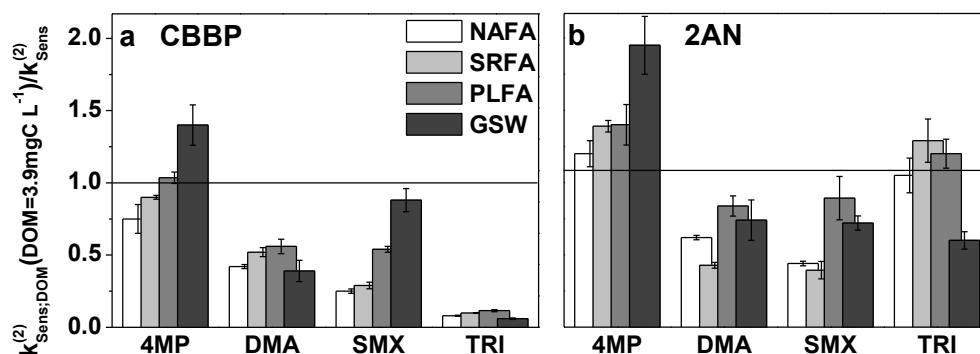
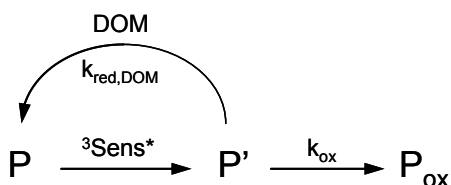


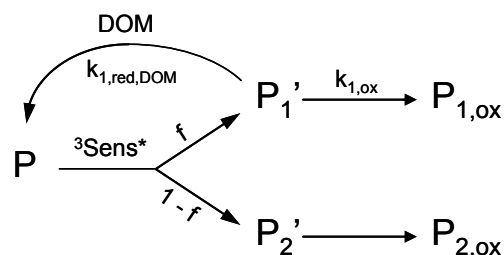
Figure 2. Ratio of reaction rates of triplet-induced oxidation in DOM free solutions to GSW and reference DOM solutions (all at 3.9 mgC L⁻¹, according to GSW concentration) for a) CBBP and b) 2AN. Error bars represent 95% confidence intervals.

Models for the DOM concentration dependence of the inhibition of oxidation. To analyze the data obtained in the present study, two kinetic models of different complexity were considered (see Scheme 1).

Scheme 1. Proposed kinetic models for the DOM concentration dependence of the inhibition of oxidation



A) One reaction channel inhibited by DOM



B) Two parallel reaction channels,
one thereof inhibited by DOM

The first model (Scheme 1A) is equivalent to the one considered in our previous paper {Canonica, 2008 #10}. The second model allows two parallel channels for the reaction of the excited triplet photosensitizer (³Sens*) with the target compound (P) to form the intermediates P₁' (with yield *f*) and P₂' (with yield (1 - *f*)). P₁' is then transformed analogously as for the above single-channel model, while P₂' is not affected by DOM and fully reacts to an oxidized product P_{2,ox}. Assuming that the corrected rate constants determined in this study can be related to these

models, one obtains eqs 6 and 7 (for details see SI Text S5) in the case of model A and B, respectively. Note that both equations do not account for triplet state quenching and are therefore not intended to be used in the case of DOM concentrations much higher than the ones used in this study, where quenching may be significant.

$$k_{Sens,DOM}^{(2)}([DOM])/k_{Sens}^{(2)} = \frac{1}{1 + \frac{k_{red,DOM}}{k_{ox}}[DOM]} \quad (6)$$

$$k_{Sens,DOM}^{(2)}([DOM])/k_{Sens}^{(2)} = \frac{f}{1 + \frac{k_{1,red,DOM}}{k_{1,ox}}[DOM]} + (1-f) \quad (7)$$

For the one-channel model, k_{ox} and $k_{red,DOM}$ are the first-order rate constant for reaction of the intermediate P' leading to P_{ox} and the second-order rate constant for reduction of the intermediate P' by DOM, respectively, and an analogous meaning holds for the parameters of the two-channel model. These kinetic constants cannot be determined experimentally by the methods applied here, but from data fitting to eqs 6 or 7 their ratio can be obtained. One can define such a ratio as $[DOM]_{1/2}$ (eq 8), which is the concentration of DOM required to reduce the observed oxidation rate constant to the half of the value in the absence of DOM.

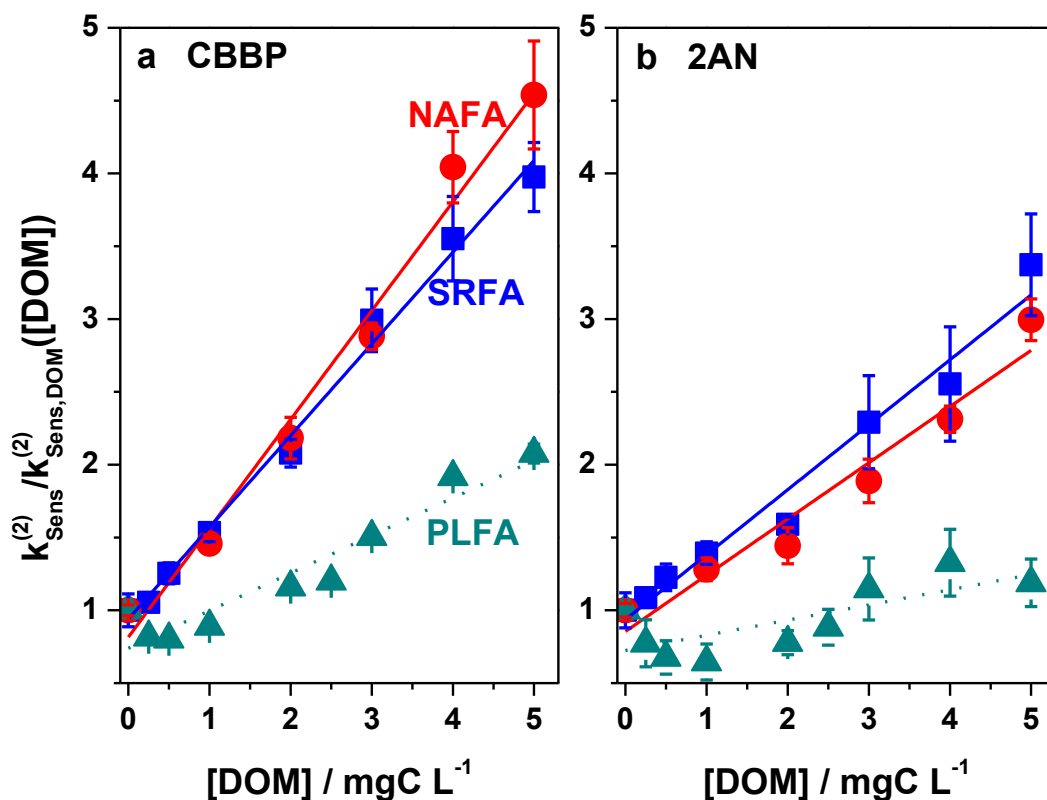
$$[DOM]_{1/2} = \frac{k_{ox}}{k_{red,DOM}} \quad (8)$$

Similar considerations hold for the two-channel model, $[DOM]_{1/2}$ referring in this case to half of the maximum reduction in oxidation rate constant. In our previous study, eq 6 was transformed by taking the inverse of both terms to get a linear relationship with respect to $[DOM]$ (eq 6a).

$$k_{Sens}^{(2)} / k_{Sens,DOM}^{(2)}([DOM]) = 1 + \frac{k_{red,DOM}}{k_{ox}}[DOM] = 1 + [DOM]/[DOM]_{1/2} \quad (6a)$$

1 **Model application to data.** As shown in Figure 3, the one-channel model and eq 6a applied
2 well for SMX oxidation in the presence of SRFA and NAFA, and regression lines for these two
3 DOMs showed a very similar slope (corresponding to the inverse of $[DOM]_{1/2}$). The fit between
4 the PLFA data and eq 6a was not satisfactory, indicating a deviation from the simple model,
5 which is apparently due to the concomitant presence of factors enhancing and inhibiting
6 oxidation of the target compounds, as already mentioned in the above qualitative discussion of
7 the data. Nevertheless, from Figure 3 it can be concluded that the net inhibition caused by PLFA
8 is much smaller than that caused by the other two fulvic acids.

1



2

3

Figure 3. Plots of inverse rate constant ratios for sulfamethoxazole (SMX) versus [DOM] and linear regression lines according to eq 6a. Photosensitizers: a) CBBP and b) 2AN. DOMs: ●, Nordic Aquatic fulvic acid (NAFA); ■, Suwannee River fulvic acid (SRFA); ▲, Pony Lake fulvic acid (PLFA).

8

For DMA and TRI only the two-channel model (eq 7) was able to yield satisfactory data fits (performed using the non-linear curve fit procedure for rational functions as provided by the Origin software version 8.0 (OriginLab)). The model curves are shown in Figures 1 and S3 of SI, and fit parameters for both models A and B are collected in Table 1. $[DOM]_{1/2}$, which is the

relevant parameter for the quantification of the inhibition of oxidation, was found to fall in the range of $0.11 - 2.85 \text{ mgC L}^{-1}$ for all systems studied. SMX showed the least efficient inhibition of oxidation, with values of $[DOM]_{1/2}$ higher for the 2AN than for the CBBP system. This might indicate the formation of different oxidation intermediates of the target compound in the two systems or a photosensitizer-specific change in the antioxidant property of DOM. In addition, the application of model B tended to somewhat increase the $[DOM]_{1/2}$ values, but did not significantly improve the fits, suggesting that the one-channel model is sufficient to describe the inhibition of SMX oxidation by DOM. For TRI, $[DOM]_{1/2}$ values were at least an order of magnitude smaller than for SMX and about half of those for DMA, meaning that, for the oxidation channel inhibited by DOM, transformation of TRI and DMA is much more effectively inhibited than that of SMX. For the systems involving PLFA, fitting parameter values from Table 1 are given in square brackets because the models appear to be too simplistic to accurately fit the data. Nevertheless markedly higher $[DOM]_{1/2}$ values for PLFA than for the other two fulvic acids, confirm the qualitative picture obtained above that PLFA is less efficient in inhibition of oxidation. As far as f , the fraction of reaction inhibited by DOM, is concerned, SMX exhibits potentially complete inhibition ($f \approx 1$) and TRI (only the system with CBBP could be analyzed) is not very far from this limit ($f \approx 0.93 - 0.95$), whereas for DMA only about one half of the reaction appears to be inhibited by DOM ($f \approx 0.42 - 0.61$). According to the model, f should be independent of the type of DOM employed for inhibition (for a given target compound/photosensitizer system), and this is generally confirmed by the data in Table 1.

Relevance to aquatic photochemistry. The results of the present study reinforce the conclusions of our previous paper {Canonica, 2008 #10} that excited triplet-induced oxidation of some aquatic contaminants can be inhibited by the presence of DOM. The usage of 2AN as a

1 model photosensitizer permitted to verify the inhibiting effect of DOM in the case of oxidation
2 by excited triplet states possessing a relatively low oxidizing strength, thus fortifying the
3 hypothesis that oxidations induced by $^3\text{DOM}^*$ should also be subject to such an inhibition by
4 DOM. It also showed some intrinsic limitations of the methodology, which become apparent
5 especially when considering the enhanced oxidation of 4MP upon DOM addition. Probably, an
6 unwanted side-reaction is introduced, which might arise from complex formation between
7 ground-state 2AN and DOM leading to an enhanced production of photooxidants. The
8 employment of negatively charged photosensitizers (such as CBBP), which tend to less complex
9 formation with DOM at circumneutral pH, could partly avoid such side-reactions but not
10 eliminate them completely, as evidenced by some increase in oxidation rates observed for the
11 system CBBP-PLFA. Despite this limitation, the use of model photosensitizers gives access to
12 valuable data for the study of indirect phototransformations of aquatic contaminants, for which
13 DOM may act not only as a photosensitizer but also as an inhibitor of their transformation.
14 Regarding this dual function of DOM, it is interesting to note that mainly allochthonous, highly
15 aromatic DOM (such as SRFA and NAFA) generally presents a higher efficiency to inhibit
16 excited triplet-induced oxidation and, at the same time, a lower photochemical reactivity (see
17 Table S3 in SI) than mainly autochthonous DOM. Similar differences in photochemical reactivity
18 were recently observed by Guerard and coworkers for $^3\text{DOM}^*$ -induced transformation of
19 sulfadimethoxine and triclocarban {Guerard, 2009 #80} {Guerard, 2009 #91} and were also
20 documented in a previous study {Canonica, 1995 #22}. It may be concluded that, particularly for
21 the contaminants affected by inhibition of oxidation, their phototransformation induced by
22 $^3\text{DOM}^*$ will be vary greatly depending on DOM type, and be quite inefficient for highly aromatic
23 DOMs.

1 **Table 1. Results of data fitting to kinetic models.** ^{a, b, c}

2

Photosensitizer		CBBP				2AN			
Target compound	Type of DOM								
A) one channel model		[DOM] _{1/2} / mgC L ⁻¹		r^2 ^d	n ^e	[DOM] _{1/2} / mgC L ⁻¹		r^2 ^d	n ^e
SMX	NAFA	1.10 (±0.23)		0.981	6	2.10 (±0.42)		0.967	6
	SRFA	1.49 (±0.13)		0.992	8	2.21 (±0.26)		0.943	8
	PLFA	[2.9]		[0.90]	9	[6.9]		[0.51]	9
B) two channel model		[DOM] _{1/2} / mgC L ⁻¹	f	r^2 ^d	n ^e	[DOM] _{1/2} / mgC L ⁻¹	f	r^2 ^d	n ^e
DMA	NAFA	0.18 (±0.06)	0.60 (±0.02)	0.964	5	0.20 (±0.06)	0.42 (±0.03)	0.973	6
	SRFA	0.28 (±0.04)	0.55 (±0.01)	0.994	6	0.13 (±0.03)	0.61 (±0.01)	0.987	6
	PLFA	[0.45]	[0.52]	[0.91]	6	[0.11]	[0.20]	[0.73]	6
TRI	NAFA	0.12 (±0.02)	0.95 (±0.01)	0.972	6	n.a.	n.a.	n.a.	5
	SRFA	0.11 (±0.05)	0.93 (±0.02)	0.954	6	n.a.	n.a.	n.a.	6
	PLFA	[0.66]	[1]	[0.94]	10	n.a.	n.a.	n.a.	6
SMX	NAFA	1.56 (±0.70)	1	0.959	6	2.85 (±1.56)	1	0.942	6
	SRFA	1.67 (±0.52)	1	0.983	8	2.82 (±1.25)	1	0.924	8
	PLFA	[5.2]	[1]	[0.74]	9	[13]	[1]	[0.23]	9

3

4 Notes: ^a Errors given in parentheses as standard deviations. ^b n.a.: Not applicable to data. ^c In case of large deviation from the model,
5 fit parameters are given in square brackets. ^d correlation coefficient (coefficient of determination). ^e number of data points included in
6 data fitting.

7

B. Oxidation induced by hydroxyl radical ($\cdot\text{OH}$)

For oxidation induced by $\cdot\text{OH}$, a possible inhibition due to interaction of SRFA used as reference DOM with oxidation intermediates was investigated by using competition kinetics (see Text S6 in SI for details). This method was employed mainly to account for scavenging of $\cdot\text{OH}$ by DOM, and second-order depletion rate constants of target compounds in the presence and absence of DOM could be determined using *para*-chlorobenzoic acid (*pCBA*), in its anionic form, as a reference compound. *pCBA* has been extensively used as a probe compound to determine $\cdot\text{OH}$ concentration and exposure in aquatic systems {Hoigné, 1997 #83} {Elovitz, 1999 #82} and its second-order rate constant for reaction with $\cdot\text{OH}$ is known: $k_{\cdot\text{OH},pCBA} = 5.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ {Neta, 1968 #84}. As a working hypothesis, $k_{\cdot\text{OH},pCBA}$ is assumed to be unaffected by the presence of DOM. When not irradiated, all sample solutions were found to be stable over the time needed for experiments and HPLC analysis. Blank experiments consisting in irradiation of aqueous solutions, with or without SRFA, containing all ingredients but hydrogen peroxide, were performed to check and possibly correct for side reactions other than oxidation by $\cdot\text{OH}$, such as direct or DOM-induced phototransformation. For the large majority of studied compounds (including the reference compound *pCBA*) no correction was made owing to the negligible depletion rates measured in blank experiments (< 5 % of overall depletion due to side reactions). In the cases where side reactions were found to be important, correction was done on the basis of observed pseudo-first-order kinetics for the depletion of the target compounds in competition kinetics and blank experiments. The correction method as well as the compounds affected by the correction are given in detail in SI (Text S6).

The bar chart in Figure 4 shows second-order rate constants ($k_{\cdot\text{OH},P}$) obtained from competition kinetics experiments for fifteen selected compounds, representing environmentally relevant

contaminants as well as model compounds. The rate constants measured in the absence of SRFA agree well with available literature values {Buxton, 1986 #85} {Huber, 2003 #8}. For most compounds, $^{\bullet}\text{OH}$ reaction rate constants did not change significantly upon addition of SRFA (2.5 mgC L^{-1}). No decrease in reaction rate was observed for any compound. Only for the x-ray contrast media iohexol and iopromide, the rate constant increased by about 25% in the presence of SRFA.

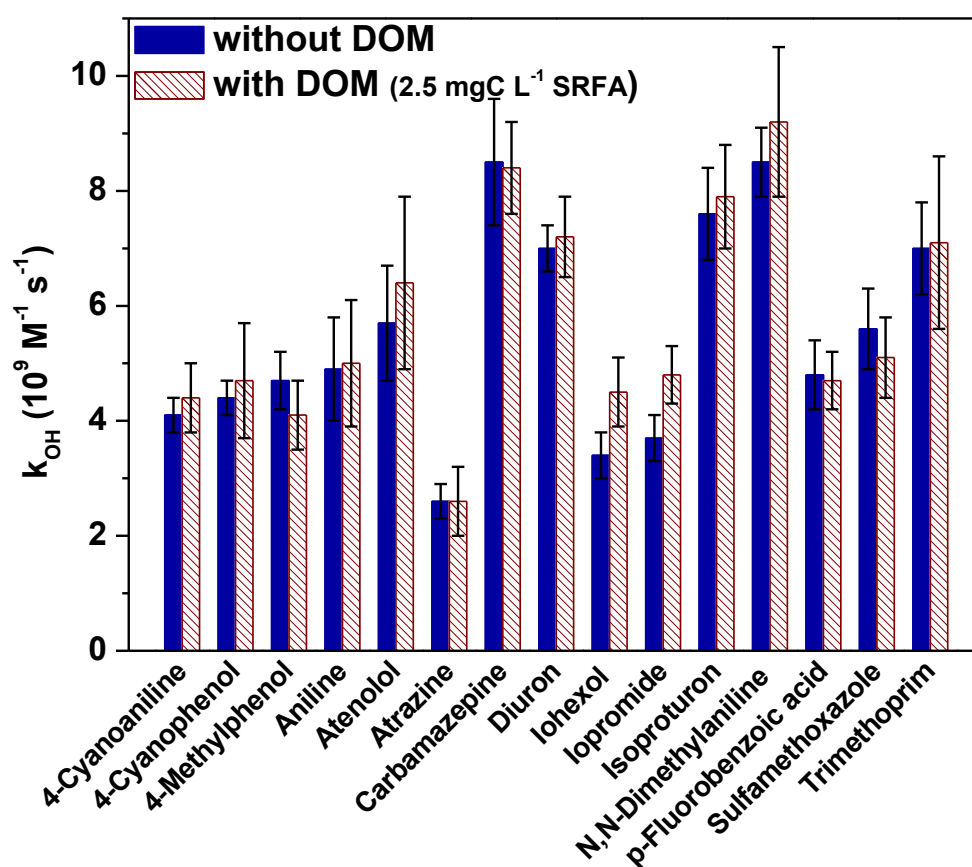


Figure 4. Second-order reaction rate constants of hydroxyl radical with fifteen target compounds in the presence and absence of SRFA (2.5 mgC L^{-1}) used as reference DOM. Error bars represent 95% confidence intervals of regression lines obtained by competition kinetics experiments.

1
2 The absence of DOM-induced inhibition effect for oxidation of the selected compounds by $\cdot\text{OH}$
3 is somewhat surprising in view of the many cases of such inhibition found for oxidation by
4 excited triplet states. It should be discussed here by considering possible reaction mechanisms.
5 With most substrates, $\cdot\text{OH}$ reacts at close to diffusion controlled rates and undergoes mainly three
6 types of reactions: Addition to double bonds and aromatic compounds, H-abstraction and less
7 frequently electron transfer {Von Sonntag, 2006 #52}. The addition of $\cdot\text{OH}$, which is the most
8 likely mechanism to occur with the studied compounds, proceeds via a reversible π -complex,
9 which then transforms to a σ -complex radical. Subsequently, the radicals are oxidized forming
10 the corresponding hydroxylated compounds {Ashton, 1995 #75; Volkert, 1968 #76}. The tight
11 C–O bond in the σ -complex formed upon $\cdot\text{OH}$ addition appears to offer no possibility to reform
12 the parent compound. For phenols, formation of phenoxyl radical intermediates after $\cdot\text{OH}$
13 addition and water elimination has also been reported {Roder, 1999 #86}, and this could lead to
14 reformation of phenol in the presence of antioxidants, but apparently such a pathway is not
15 relevant under the experimental conditions of the present study. An increased reactivity of
16 iodinated contrast media in the presence of DOM, possibly connected to the increase in $\cdot\text{OH}$ -
17 induced reactivity found here, has been previously observed for ozonation of river water {Huber,
18 2003 #8}. Finally, in view of the quite variable extent of the inhibition effect observed with
19 triplet-induced oxidation {Canonica, 2008 #10} and the absence of DOM effect on the $\cdot\text{OH}$
20 competition kinetics rate constants obtained for almost all compounds studied here, it appears to
21 be quite unlikely that the used reference compound, *p*CBA, is subject to interference by DOM in
22 its depletion induced by $\cdot\text{OH}$. Furthermore, this is confirmed by many studies in which *p*CBA
23 served as a probe compound to predict the relative elimination of micropollutants in natural

waters during ozonation and AOPs based on the second-order rate constants measured in ultrapurified water {Huber, 2003 #8} {von Gunten, 2003 #92}. Thus, no contraindication to the use of *p*CBA as a probe compound to determine $\cdot\text{OH}$ concentrations in the presence of DOM can be derived from this study.

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Supporting Information Available

5 texts, 3 tables and 4 figures are available for further information addressing materials, experimental procedures, calculations and additional data. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited